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(54) **Pattern forming method.**

(57) Disclosed is a pattern forming method wherein (i) an organic thin film is formed on a semiconductor substrate, (ii) this organic thin film is selectively exposed with a first deep UV light (excimer layer light of 248 nm) to degenerate only the vicinity of the surface of the organic thin film (where the degenerated part possesses the property for absorbing the wavelength of the light of second exposure), (iii) the entire surface of the organic film is irradiated with a light having a waveform with excellent transmissivity of the organic thin film (e.g. g-ray of 436 nm), and (iv) the organic thin film is developed and removed except for the part degenerated by the first exposure, thereby forming a pattern. According to this method, fine processing in fabrication of semiconductor device of the like can be effected easily, and, still more, a superfine pattern (e.g. 0.5  $\mu$ m or less) can be presented.

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## PATTERN FORMING METHOD

## Background of the Invention

This invention relates to a pattern forming method and, more particularly to a pattern forming method for a new and simple pattern forming which is capable of providing superfine pattern by simple process.

The recent advancement in semiconductor device manufacturing technology has given rise to demand for photolithographic technology for forming superfine pattern in the order of 0.5 micron meter. As the technology for forming superfine pattern of 0.5 micron meter or even smaller, in the aspect of apparatus, studies of techniques for shortening the wavelength and widening the aperture of the conventional stepper are promoted. Besides, as new devices for forming superfine patterns, excimer laser stepper, X-ray stepper, and direct drawing type electron beam exposure apparatus are being developed. Moreover, various methods are proposed and attempted in the resist process technology, too. For example, multilayer resist method (MLR method), antireflective coating method (ARC method), contrast enhanced lithography method (CEL method), portable conformable mask method (PCM method), and image reversal method (IR method) are known.

There is, however, a definite limit to the widening of aperture and shortening of wavelength in the conventional stepper (i), the mask fabrication is difficult in the X-ray stepper (ii), and the throughput is low in the direct drawing type electron beam exposure device (iii). Because of these reasons, the excimer laser stepper is presently considered to be the most hopeful one. But the excimer laser stepper has its own demerits. That is, as expressed in the following Rayleigh's equation.

$$R = k\lambda/NA \dots\dots\dots (1)$$

R: resolution, k: constant (0.8 to 0.8),

$\lambda$ : exposure wavelength, NA: number of apertures of lens

when it is desired to improve the resolution without changing the wavelength, the NA must be increased, but when the value of NA is increased, the focal depth (FD) becomes shallower as shown in equation (2).

$$FD = \lambda/(NA)^2 \dots\dots\dots (2)$$

On the other hand, various methods are attempted, as stated above, in the resist process technology. In any of these methods, although it was effective to compensate for deterioration of focal depth in the photolithographic process, but they were not practical enough because the process was complicated or the effect of expansion of focal depth was not sufficient.

That is, in the conventional resist process technology, it was not enough to cope with the shallow focal depth due to shortening of wavelength and widening of aperture in the excimer laser stepper.

## Summary of the Invention

It is hence a primary object of this invention, in the light of solving the above-discussed problems of the conventional resist process, to present a pattern forming method in the resist process technology capable of fully exhibiting the performance of the exposure device with a shallow focal depth as in excimer laser stepper.

This and other objects are accomplished by a pattern forming method which includes a step of forming an organic thin film on a substrate such as semiconductor substrate by applying an organic coat film material comprising an organic materials of which chemical property is changed by a first exposure and an organic material of which chemical property is changed by a second exposure, a step of selectively exposing the vicinity of the surface of said organic thin film by said first exposure, a step of exposing the entire surface of said organic thin film by said second exposure, and a step of forming a pattern by developing said exposed organic thin film.

In an illustrative embodiment, the organic coat film material is, for example, made of alkaline soluble resin primarily, containing, furthermore, an organic material made of aromatic azide compound which chemically changes at the wavelength of first exposure and diazo compound which chemically changes at the wavelength of second exposure.

This invention also relates to a pattern forming method which includes a step of applying an organic thin film of which chemical property is changed responding to a first energy beam on an arbitrary substrate, a step of selectively exposing the vicinity of the surface of said organic thin film by said first energy beam, a step of depositing a substance for absorbing a second energy beam selectively on the exposed part of

the surface of said organic thin film, a step of exposing the entire surface of said organic thin film by said second energy beam, and a step of forming a pattern by developing said exposed organic thin film.

According to the present invention as described herein, the following benefits, among others are obtained.

5 The pattern forming method of this invention realizes the resist process making use of only the advantageous points of all of MLR, CEL, PCM, IR and other methods.

That is, for the primary energy beam exposure, for example, only the vicinity of the surface of positive resist is used, and it is exposed selectively by deep UV light (for example, KrF excimer light; 248 nm) so as to degenerate only the vicinity of surface of said resist. In the next step, the above degenerated portion is  
10 selectively stained with a chemical substance which absorbs the light of secondary energy beam exposure, for example, dyestuff. Then, the entire surface is exposed by, for example, UV light which is excellent in transmissivity to the resist as secondary energy beam, and the positive resist is developed and removed, leaving only the already stained portion. Namely, according to the resist pattern forming method of this invention;

15 (1) Since only the very thin portion near the surface of positive resist is selectively exposed by first exposure, the advantage of MLR is utilized.

(2) By staining the selectively exposed portion, the contact mask effect of CEL process is utilized.

(3) By selectively forming a light absorption pattern on the resist, the advantage of PCM is utilized.

(4) By forming a positive resist pattern by second full surface exposure, the effect of IR method is  
20 also utilized.

While the novel features of the invention are set forth with particularity in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

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#### Brief Description of the Drawings

Fig. 1 to Fig. 6 are process sectional views to explain a pattern forming method in a first embodiment of this invention; and

30 Fig. 7 to Fig. 11 are process sectional views to explain a pattern forming method of a second embodiment of this invention.

#### Detailed Description of the Invention

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Referring now to Fig. 1 to Fig. 6, a first embodiment of pattern forming method and pattern forming materials of this invention is described below.

First, as shown in Fig. 1, an organic thin film 2 is formed on an arbitrary substrate (for example, a semiconductor substrate) 1 by coating with an organic coating material in a thickness of 1 to 2 microns  
40 meter. Said organic coating material is primarily composed of alkaline soluble resin (for example, phenol novolak resin), and contains, as photosensitizers, diazo compound (for example, 1,2-naphthoquinone diazide sulfonic chloride) and aromatic azide compound (for example, 2-phenylamino-5-azidebenzoic acid). In succession, as a first exposure, the vicinity of the surface of said organic thin film 2 is selectively exposed with far ultraviolet ray (for example, KrF excimer laser light) 3 (Fig. 3). Here, numeral 4 denotes a photo  
45 mask for selective exposure. At this time, since the principal component of the organic thin film 2 absorbs the majority of the far ultraviolet ray, only the surface layer in a thickness of 0.1 to 0.2 microns meter of the organic thin film 2 is exposed in a pattern, and a very thin exposure part 5 is formed only on the surface. Therefore, in this step, the same effect as in the multilayer resist is obtained, that is, the effect is the same as when thin resists are overlaid and only the top layer resist is exposed selectively. Namely, an exposure  
50 apparatus with shallow focal depth and high resolution can be used, and a sharp superfine pattern of 0.5 micron meter or less with a high resolution can be obtained (Fig. 3).

Here, the aromatic azide compound (for example, 2-phenylamino-5-azidebenzoic acid) reacts photochemically with far ultraviolet light (for example, excimer laser light), and its color changes from green to black depending on the exposure time. That is, the extremely thin exposure part 5 of the surface only  
55 above forms a colored part 6 which is colored by said compound. At this time, the colored part 6 absorbs all light with wavelength of at least 450 nm or less (Fig. 4). Therefore, when the entire surface is exposed by using light 7 with longer wavelength than said far ultraviolet light in a second exposure, for example, light with wavelength of 450 nm or less (for instance, g-ray of 436 nm), only the uncolored portion 8 of the

organic thin film 2 is selectively exposed (Fig. 5). In this step, using the colored part 6 as the mask, the uncolored part 8 which is in contact with the colored part 6 is exposed, and this is a contact exposure of so-called mask contact type. Therefore, pattern exposure of high fidelity to the mask and high precision may be performed. That is, in this step, the three effects of the CEL method, PCM method, and IR method are taken in at the same time.

Finally, by developing the organic thin film with developing solution (for example, an aqueous solution of quaternary amine compound, such as tetramethyl ammonium hydroxide), only the uncolored part 8 is removed, and the colored part 6 only is left over as resist pattern 9. Same as in the IR method, a high resolution pattern of about 0.5 micron meter opposite to the mask pattern is obtained (Fig. 6).

In this embodiment, KrF excimer laser light was used in the first exposure and g-ray as the second exposure, but the wavelengths of the first and second exposures may freely changed by the combination of light absorbing regions of the diazo compound and aromatic azide compound which are photosensitizers making up the organic coating material.

Besides, in the illustrated example, the colored part was formed selectively only on the exposed part, but, to the contrary, it is evident that the same effect is obtained, except that the pattern is inverted, when only the exposed part is decolored by causing chemical change on the colored part in the vicinity of the surface of the organic thin film by the wavelength of the first exposure, using an organic film on which a colored part is preliminarily formed entirely.

Furthermore, the light of the first exposure is not limited to excimer laser light, but X-ray, electron beam, ion beam and others may be used, and the light of the second exposure is not limited to g-ray, but i-ray, visible ray, soft X-ray and others may be used.

In the method of this embodiment, in the pattern-shaped first exposure, since only the surface portion of the organic thin film 2 is used, the exposure apparatus is widened in the aperture and shortened in the wavelength, and it is sufficiently usable if the focal depth becomes shallow, so that the resolution of the apparatus can be fully exhibited.

Furthermore, as compared with the conventional multilayer resist method (MLR method) process, only one coating step is enough, and the development is also needed in one step, so that the manufacturing process may be notably simplified.

Still more, as compared with the conventional image reverse method (IR method) process, heat treatment is not needed in the pattern forming method of this invention, so that the process stability is enhanced.

Moreover, since the pattern forming method of this embodiment does not require formation of photo bleaching film on the resist surface as required in the conventional contrast enhanced method (CEL method) process, so that the exposure time is significantly shortened, while the contrast is sufficient and coating is needed only in one step.

What is more, as compared with the conventional antireflection coating method (ARC method) process, only the vicinity of the surface of organic thin film is exposed, and the exposure light does not reach the lower part of the organic thin film, which means there is no reflection from the substrate surface, so that the pattern resolution may be notably enhanced.

In addition, the pattern forming method of this embodiment, as compared with the conventional portable conformable method (PCM method) process, is capable of forming a light absorption layer in a pattern shape of high contrast on the surface of resist without coating in two layers, so that the resolution of the resist pattern may be greatly improved. And many other effects are obtained.

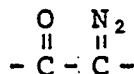
Thus, the pattern forming method and pattern forming materials of this embodiment are effective to obtain a sufficiently high resolution, being applied to an exposure apparatus with shallow focal depth, such as excimer laser stepper, without making and drastic modification as compared with the conventional photo resist process technology.

Next is explained a second embodiment of this invention by reference of the process sectional views shown in Fig. 7 to Fig. 11.

First, as shown in Fig. 7, an arbitrary substrate, for example, a semiconductor substrate (e.g. Si substrate) 10 on which a semiconductor wafer, that is, SiO<sub>2</sub> 40 is formed is coated with an ordinary positive resist 11 [for example, AZ1400, AZ4000, AZ5200 (all made by Hoechst)] in a thickness of 1 to 2 μm. Next, as a first exposure, deep UV light (far ultraviolet ray, such as KrF excimer light) 12 is selectively emitted for a short time to expose the vicinity of the surface of the positive resist 11 selectively (Fig. 8). At this time, since the main polymer of the positive resist 11 absorbs the majority of deep UV light, if slightly overexposed, the positive resist 11 is selectively exposed in a pattern shape only in the surface layer in a thickness of 0.1 to 0.2 μm, so that an extremely thin exposure pattern 20 is formed. Therefore, in this step, the same effect as in the multilayer resist, that is, lamination of thin resist layers and selective exposure of

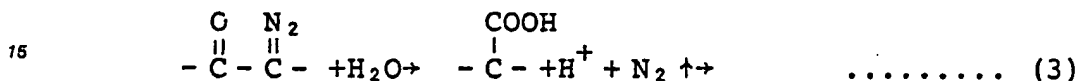
only the top layer resist, will be obtained. Namely, an exposure apparatus of shallow focal depth and high resolution can be used, and a sharp and high resolution superfine pattern 20 of 0.5  $\mu\text{m}$  or less in width may be obtained.

The surface layer 20 of the positive resist selectively exposed in the above step contains, as a  
5 photosensitive material, a reagent including a



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group of naphthoquinone diazide compound, and photoreaction of formula (3) occurs only by exposure.



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Therefore, only the -COOH group produced by this primary exposure is selectively stained with an ordinary alkaline dyestuff (such as fuchsin for red color, auramine for yellow, and aniline black for black),  
20 and a stained layer 30 is formed (Fig. 9). At this time, the alkaline dyes of red, yellow and black absorb all light with wavelength of at least 450 nm or less. Therefore, in the secondary exposure, when the entire surface is exposed by using light with longer wavelength than that of above deep UV light, for example, light 13 with wavelength of 450 nm or less, only the unstained portion 200 of the resist 11 can be selectively exposed (Fig. 10). That is, in this step, the three effects of CEL method, PCM method and IR  
25 method are taken in simultaneously.

Finally by developing with a developing solution of positive resist, only the unstained portion 200 is removed, and, same as in the IR method, a high resolution resist pattern 14 of about 0.5  $\mu\text{m}$  opposite to the mask pattern may be used by using the positive resist (Fig. 11).

In this embodiment, KrF excimer light was used in the first exposure and UV light in the second  
30 exposure, but depending on the selection of resist, light of same wavelength may be used in the first and second exposures.

For pattern staining, meanwhile, alkaline dyes were used, but it is obvious that they are not limitative as far as it is possible to absorb the light of second exposure and deposit selectively on the exposure pattern part, and for example aniline may be used because it can absorb light of g-ray.

Besides, only the exposed part was selectively stained in the above illustrated example, but it is obvious that the same effects will be obtained when the other portion than the exposed part is stained except that the pattern is inverted. Similarly, the light of the first exposure is not limited to excimer laser light, by X-ray, electron beam, ion beam and others may be used, and the light of the second exposure is not limited to g-ray, but i-ray, visible ray, soft X-ray and others may be used.  
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Furthermore, the organic thin film is not limited to the positive resist, and any other material such as polycarbonate resin can be used as far as it can cause chemical reaction by the first energy beam and selectively deposit that substance that does not absorb or pass the second energy beam.  
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In this embodiment, since the pattern shaped primary exposure is used only on the resist surface, it is sufficiently usable if the exposure apparatus is higher in NA and shorter in wavelength, and shallow in the  
45 focal depth, whereas the resolution of the apparatus can be fully exhibited.

That is, as compared with the conventional multilayer resist process (MLR method), only one step of coating is enough. To remove the resist, moreover, only one step of development is enough, and the manufacturing process may be significantly simplified.

Besides, as compared with the conventional image reversal process (IR method), since heat treatment  
50 is not needed, the process stability is excellent.

Moreover, unlike the contrast enhanced lithography method (CEL method), there is no light bleached film on the resist, and the exposure time is notably shortened, and the contrast is sufficient, and only one step of coating is enough.

What is more, as compared with the antireflection coating method (ARC method), only the vicinity of the  
55 resist surface is exposed, and the pattern exposure light does not reach to the lower part of the resist, so that there is no reflection from the substrate surface, thereby greatly enhancing the pattern resolution.

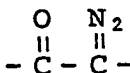
Still more, as compared with the portable conformable mask (PCM) method, it is not necessary to coat in two layers, and a pattern shaped light absorption layer of high contrast can be formed on the resist

surface, so that the resist pattern may be dramatically enhanced. And many other effects are expected.

While specific embodiments of the invention have been illustrated and described herein, it is realized that other modifications and changes will occur to those skilled in the art. It is therefore to be understood that the appended claims are intended to cover all modifications and changes as fall within the true spirit  
5 and scope of the invention.

## Claims

- 10 1. A pattern forming method comprising:  
a step of forming an organic thin film of which chemical property changes responding to a first energy beam on a substrate;  
a step of forming a region for absorbing selectively a second energy beam on the surface of said organic thin film by selectively exposing the surface of said organic thin film with said first energy beam;  
15 a step of exposing the entire surface of said organic thin film with said second energy beam; and  
a step of forming a pattern by developing said exposed organic thin film.
2. A pattern forming method of claim 1, wherein the layer to absorb the second energy beam is formed as the substance in the organic thin film is chemically changed by the first energy beam exposure into a substance for absorbing the second energy beam.
- 20 3. A pattern forming method of claim 2, wherein the organic coat film material to form the organic thin film is primarily composed of alkaline soluble resin, and contains an organic material which chemically changes at the wavelength of the first energy beam and an organic material which chemically changes at the wavelength of the second energy beam.
4. A pattern forming method of claim 3, wherein the organic material which is changed by the light of  
25 the wavelength of the first energy beam is made of an aromatic azide compound, and this organic material is composed of an organic material which is not chemically changed by the light of the wavelength of the second energy beam but is chemically changed by the light of the wavelength of the first energy beam into a substance for absorbing the wavelength region of the second energy beam.
5. A pattern forming method of claim 3, wherein the organic material which is changed by the light of  
30 the wavelength of the second energy beam is made of diazo compound.
6. A pattern forming method of claim 1, wherein the layer for absorbing the second energy beam is formed by depositing the substance on the surface of the organic thin film selectively exposed by the first energy beam.
7. A pattern forming method of claim 1, wherein the organic thin film is a positive resist.
- 35 8. A pattern forming method of the claim 6, wherein the substance for absorbing energy beam is a dyestuff.
9. A pattern forming method of claim 6, wherein the dyestuff is an alkaline dyestuff.
10. A pattern forming method of claim 6, wherein the positive resist contains a



- 40 group.
- 45 11. A pattern forming method of claim 1, wherein the first and second energy beams are ultraviolet rays.
12. A pattern forming method of claim 1, wherein the wavelength of the first energy beam is longer than that of the second energy beam.
13. A pattern forming method of claim 1, wherein the first energy beam is a far ultraviolet excimer light.
- 50 14. A pattern forming method comprising:  
a step of forming an organic thin film of which chemical property changes responding to a first energy beam on a substrate, with said organic thin film being primarily composed of alkaline soluble resin, containing diazo compound and aromatic azide compound as photosensitizers;  
a step of forming a colored region on the surface of said organic film by selectively exposing the  
55 surface of said organic film with said first energy beam;  
a step of irradiating the entire surface of said organic film with a second energy beam, thereby the other portion of the organic thin film than the colored region, with the colored region acting as the mask;

and

a step of forming a pattern by developing said organic thin film and removing the other portion than said colored region.

15. A pattern forming method of claim 14, wherein said diazo compound is 1,2-naphthoquinone diazidesulfonic chloride, and aromatic azide compound is 2-phenylamino-5-azide benzoic acid.

16. A pattern forming method comprising:

a step of forming an organic thin film of which chemical property changes responding to a first energy beam on a substrate;

a step of selectively exposing the surface of said organic thin film with said first energy beam;

10 a step of coloring the exposed part of said organic film to form a colored part;

a step of irradiating the entire surface of said organic film with a second energy beam, thereby exposing the organic thin film using said colored part as the mask;

and a step of forming a pattern by developing said organic thin film and removing the exposed part by said second energy beam.

15 17. A pattern forming method of claim 16, wherein said organic film containing a main polymer which absorbs the first energy beam is formed by positive resist, and the colored part is formed as being stained with a dyestuff.

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FIG. 1

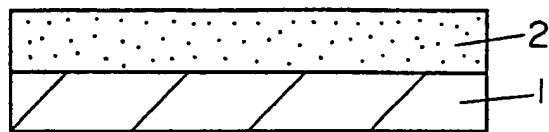


FIG. 2

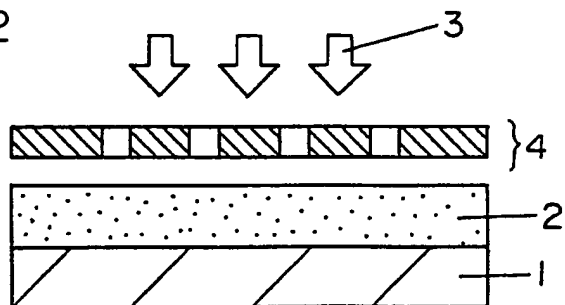


FIG. 3

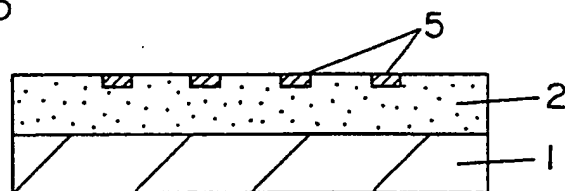


FIG. 4

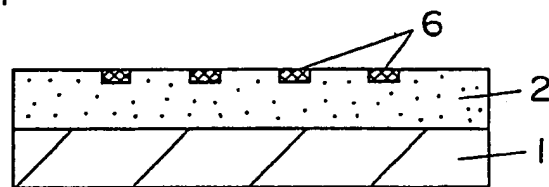


FIG. 5

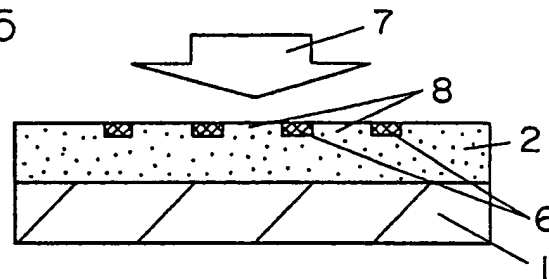




FIG. 6

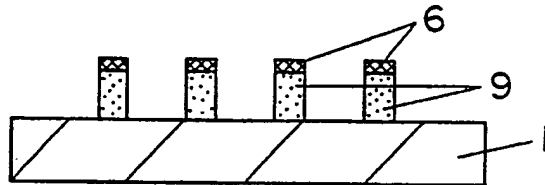


FIG. 7

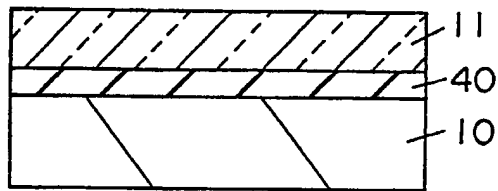


FIG. 8

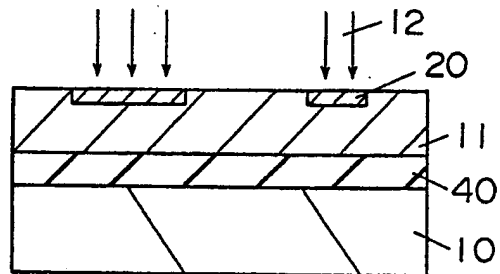


FIG. 9

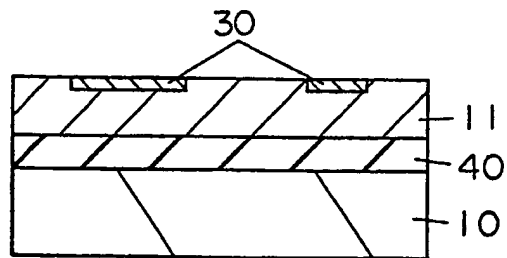


FIG. 10

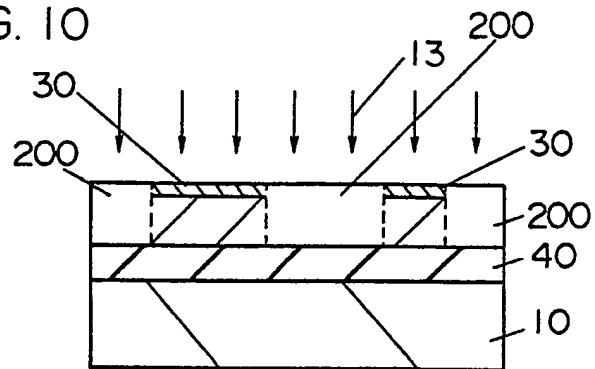


FIG. 11

